

HETEROATOM SPECIES IN COAL LIQUEFACTION PRODUCTS

F. K. Schweighardt, C. M. White, S. Friedman and J. L. Shultz

Energy Research and Development Administration
Pittsburgh Energy Research Center
4800 Forbes Avenue, Pittsburgh, PA 15213

INTRODUCTION

An assessment of the nitrogen and oxygen heteroatom species in coal-derived products is a complex yet important analytical problem in fuel chemistry. Principally, this is because the system is a multifarious molecular mixture that does not easily lend itself to direct analysis of any one component or functional group. Albeit this problem is not new, the characterization of these heteroatoms is of immediate importance to further processing of these fuels. We shall detail the methods and techniques used to rapidly isolate and/or characterize both nitrogen and oxygen heteromolecular species. Utilization is made of solvent separations, functional group type separation, chemical derivatization, HCl salt formation and the use of chromatographic and spectrometric analytical methods to quantitate our results. Specifically, we ascertained the kind and distribution of nitrogen and oxygen heteromolecules in a coal liquefaction product and in a recycle solvent used in solvent refined coal (SRC) processing. The coal liquefaction product was first solvent separated into oils, asphaltenes, preasphaltenes and ash, while low boiling oils (light oils) trapped from knock-out tanks and the SRC recycle solvent were treated directly. Nitrogen bases were complexed as HCl adducts or separated on ion-exchange resins. Hydroxyl-containing species from the separated fractions were quantitated by infrared spectroscopy or by formation of a trimethylsilyl ether (TMS) and subsequent analysis by ^1H NMR and mass spectrometry. Hydroxyl species were also isolated on ion-exchange resins or by selective gradient elution from silica gel.

EXPERIMENTAL

Solvent Separation

Coal liquefaction products were solvent separated¹ by first freezing the coal liquids in liquid nitrogen and grinding them to fine particles. This frozen oil can be easily transferred to a stainless steel centrifuge tube. Pesticide grade solvents were then used to solubilize specific fractions--oils (pentane), asphaltenes (benzene), preasphaltenes² (tetrahydrofuran) and coal-derived ash (insoluble in all solvents used). By starting with a 3-4 gram sample, one (1) liter of each solvent in four or five 200 ml portions was usually sufficient to extract the solubles. Insolubles were removed by centrifugation at 10^4 rpm at 6°C for 10 minutes. Solvents were removed by nitrogen flush on a Rotovap using a water bath ($65\text{--}85^\circ\text{C}$). Asphaltenes were treated differently at the final solvent removal step; a 20 ml solution of benzene/asphaltenes was swirled in a flask and flash frozen in liquid nitrogen, and the solvent was sublimed at $10^{-1}\text{--}10^{-2}$ torr for 2-3 hours.

HCl Treatment

The objective of this procedure was to separate and/or concentrate both nitrogen heteromolecules and hydroxyl-containing species from coal-derived material.³ Gaseous HCl was bubbled through a benzene or pentane solution of the coal product to form an insoluble HCl adduct with molecules containing a basic nitrogen atom. The adduct, after being washed free of other components, was back titrated with dilute NaOH solution to free the base nitrogen into an organic phase, usually diethyl ether, methylene chloride or benzene. The two fractions recovered contain acid/neutral and nitrogen base material, respectively.

Hydroxyl Silylation

Oils, asphaltenes and preasphaltenes were treated with hexamethyldisilazane (HMDS) to form a trimethylsilyl ether (TMS) of active hydroxyl groups.^{4,5} A 50 mg sample of coal-derived product was dissolved in 25 ml of benzene containing 50 μ l of pyridine- d_5 . To this solution 500 μ l each of HMDS and N-trimethylsilyldimethylamine were added. This mixture was maintained as a closed system except for a small Bunsen valve and mildly refluxed for one hour with occasional swirling of the flask. After the reaction was completed, solvents and unreacted reagents were removed under nitrogen flush on a Rotovap and finally freeze dried from 5 ml of benzene for 30 minutes. A portion of the final product was checked by infrared spectroscopy (IR) for disappearance of the OH band at 3590 cm^{-1} .⁶ The remaining sample was dissolved in benzene- d_6 and its proton NMR spectrum taken and integrated. From the relative areas of the peaks in the proton NMR spectrum, a percent H as OH was calculated (Equation 1).

$$\frac{\left(\frac{\text{TMS Area}}{9}\right)}{\left(\frac{\text{TMS Area}}{9}\right) + (\text{Remaining Proton Area})} \times 10^2 = \% \text{ H as OH} \quad (1)$$

From an elemental analysis of the original sample, one can calculate the weight percent oxygen as OH on a moisture and ash free basis (MAF).

Combined Gas Chromatography-Mass Spectrometry (GCMS):

The combined GCMS analyses were performed using a Dupont 490 mass spectrometer* interfaced to a Varian 1700 Series gas chromatograph, equipped with an 80:20 glass splitter and a flame ionization detector. The spectrometer was also coupled to a Hewlett-Packard 2100A computer used for spectrometric data storage and reduction. The mass spectrometer was operated at a resolution of 600 and an ionizing voltage of 70 eV. The ion source, jet separator and glass line from the chromatograph to the mass spectrometer were held at 275°C. The chromatographic effluent was continuously scanned at a rate of four seconds per decade by the mass spectrometer.

The gas chromatographic separations were effected using a variety of conditions. The nitrogen bases and acid fractions from the coal liquefaction product were chromatographed on a 10' x 1/4" OD glass column packed with 100-120 mesh Supelcoport coated with 3% OV-17. Bases from the SRC product were chromatographed on a 10' by 1/8" OD glass column packed with 100-120 mesh Chromasorb-G coated with 2% OV-17. Gas chromatographic separation of bases from the light oil was achieved using a 10' x 1/8" OD glass column containing acid washed and silyl treated 100-120 mesh Supelcoport coated with 3% Carbowax 20M. In each case the He flow rate was 30 cc/min and the analyses were performed using appropriate temperature programming conditions.

Column Chromatographic Separation

Coal-derived liquids, soluble in pentane, were separated into five fractions: acids, bases, neutral nitrogen, saturate hydrocarbons and aromatic hydrocarbons. Acids were isolated using anion-exchange resins, bases with cation-exchange resins, and neutral nitrogen by complexation with ferric chloride adsorbed on Attapulugus clay. Those pentane soluble hydrocarbons remaining were separated on silica gel to give the non-adsorbed saturates and the moderately retained aromatics. This method is commonly referred to as the SARA technique.⁸

* Reference to specific makes or models of equipment does not imply endorsement by the U. S. Energy Research and Development Administration.

RESULTS AND DISCUSSION

The centrifuged coal liquid product (CLP) was produced using Ireland Mine, Pittsburgh seam, West Virginia coal in the 1/2 ton per day SYNTHOIL Process Development Unit (PDU).⁹ Operating conditions for this experiment were 4000 psi hydrogen pressure, 450°C and no added catalyst. The light oils were derived from a catalytic experiment (Harshaw 0402T) using Homestead Mine, Kentucky coal, under 4000 psi pressure and 450°C.

The coal liquefaction product was solvent separated by the method previously described to yield the distribution of fractions given in Table 1. Figure 1 gives the atom weight percent distribution of nitrogen and oxygen in the solvent separated fractions listed in Table 1. The pentane soluble oils were subsequently separated into five fractions using the SARA chromatographic scheme. Table 2 lists the weight percents of the individual fractions. The asphaltenes were treated with HCl to form acid/neutral and base subfractions, 63 and 37 weight percent, respectively.

The acid and base fractions from the SARA separation of the oils were subjected to analysis by combined GCMS and low voltage low resolution mass spectrometry (LVLR). Figures 2 and 3 reproduce the gas chromatograms of the base and acid fractions, respectively. The oxygen containing species shown in Figure 3 have been classified as alkylated phenols, indanols/tetralinols, phenyl phenols, and cyclohexyl phenols. Table 3 lists the carbon number range and tentative compound type assignments for the nitrogen heteromolecules in the acid and base fractions as determined by LVLR mass spectrometry.¹⁰ Table 4 lists the compound types assigned to the base fraction of the oils by GCMS.

Table 5 lists the carbon number range data from the HRMS analysis of the asphaltenes and their acid/neutral and base subfractions.¹¹ It must be noted that at the operating conditions of the solids inlet, 300°C, 10⁻⁶ torr, less than 50% of these materials could be volatilized. These preliminary studies have also indicated the presence of a limited number of diaza-species from Z# = 8-18.

The SYNTHOIL PDU contains several knock-out traps that condense low boiling components, light oils.¹¹ Nitrogen bases in the light oils were isolated by their precipitation with gaseous HCl and back titrated with NaOH into diethyl ether. These nitrogen bases constituted 3% by weight of the light oils. The gas chromatographic profile of these bases is given in Figure 4. An earlier study of these light oils characterized the saturates, aromatics and acidic components separated by Fluorescence Indicator Analysis (FIA).¹² The present investigation has resulted in the first quantitative analysis of pyridines and anilines in an oil produced by the hydrogenation of coal.

Table 6 summarizes the quantitative results from the chromatogram of Figure 4. It is of interest to point out that during this investigation, though numerous substituted pyridines were quantitated, no evidence for the parent was found. Because the techniques employed recovered components with boiling points near that of pyridine it is suggested that this observation may be significant. If free pyridine was trapped within the coal macromolecular structure it surely would have been found in either the light oils or the pentane soluble oils. If, on the other hand, pyridine was attached exo-, via a single C-C bond, to a more complex molecular network, the hydrogenation process should have freed it intact. But if the nitrogen heteroatom was an integral part of the original coal macromolecule, then hydrogenation would have cleaved a number of C_α-C_β bonds to produce a wide distribution of methylpyridines. Table 6 shows this methyl substitution trend. Quantitative results indicate that 2,3,6-trimethylpyridine is seven times more abundant than 2,3-dimethylpyridine and approximately twice as abundant as any other methylpyridine.

The source of anilines and, in particular, the observation of both the parent and the methyl substituted anilines are of interest. Anilines can arise from hydro-

generation of the heteroring in a fused ring system followed by breaking of the bond between nitrogen and an aliphatic carbon.¹³ Therefore quinoline and its alkyl derivative could be a source of the anilines. Table 4 lists seven quinolines found in the oils that could be the precursors. The presence of the parent aniline, that should readily be hydrogenated,¹³ is significant. If dealkylation was the same for all species, why didn't we see any of the parent pyridine? It could mean that the potential aniline moieties are located near the periphery of the coal macromolecule in contrast to the pyridines. The quantitative results indicate that methylanilines (toluidines) are in abundance in the order meta > ortho >> para > parent aniline, and all are greater than the dimethylanilines. These interpretations are based upon the more detailed analysis of the light oils. To date direct evidence for the presence of significant amounts of alkylated anilines and pyridines in the pentane soluble oils from the CLP have not been reported.

To complete this initial investigation of nitrogen species we chose to look at the nitrogen compounds present in the recycle solvent used for SRC processing and compare them with those found in coal liquefaction product oils. After extracting the gross benzene solubles, they were treated with HCl to isolate nitrogen bases. This particular sample had a slight residue that was benzene insoluble. Figure 5 gives the gas chromatographic profile of these nitrogen bases and summarizes the prominent structural isomers. The base fraction from the SRC solvent was less complex than the nitrogen bases found in the liquefaction oils, but the same principal molecular species were found in both samples.

The presence of hydroxyl groups in coal-derived materials has long been established. Our present interest is to define quantitatively the OH as a percentage of the total oxygen. The separation methods described concentrate a high percentage of the hydroxyl groups by anion exchange resin chromatography (acids) or the HCl treatment (acid/neutral). Once the separation/concentration has been made the sample is treated with a derivatizing reagent to form a trimethylsilyl ether, Ar-O-Si(CH₃)₃.

It has been shown that all of the hydroxyl groups contributing to the 3590₆cm⁻¹ infrared band can be quantitatively removed with the derivatizing reagent. The TMS ethers are next examined by proton NMR. The signals near 0 ppm represent the trimethylsilyl (CH₃)₃ protons from each of the hydroxyl derivatives. By integrating the area under the total proton spectrum and allowing for the 9-fold intensity enhancement for the TMS area, the percent H as OH can be calculated. Table 7 lists some representative determinations of hydroxyl content from oils and asphaltenes. The silyl derivatization quantitation of hydroxyls in asphaltenes has been compared to the infrared spectroscopic method of standard additions.¹⁴ Our results agreed¹⁵ to within 10%. Infrared data, and those from others working on similar fractions indicates that there is little if any carbonyl oxygen (C=O) present in coal liquefaction products produced in the SYNTHOIL PDU. Therefore, we conclude that substantially all of the oxygen exists as either hydroxyl (phenolic or benzylic) or in an ether linkage (e.g. furan).

A useful corroboration of the NMR data and of characterizing the acid fraction of the oils is its mass spectrum before and after TMS derivatization. Figure 6 A and B shows the acid components from the pentane soluble oils before and after TMS derivatization, respectively. Note that the mass peaks are shifted 72 amu to give a nearly identical mass distribution. Table 8 lists those hydroxyl containing compounds that definitely formed a TMS ether. From the mass spectral data there was also evidence for trace amounts of indenol, naphthol and phenanthrol derivatives.

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Table 1. Solvent Separation Weight Percent Distribution.

Solvent Fraction Wt. % of CLP

Oil 68.0

Asphaltenes 26

Preasphaltenes 4

Ash 2

Table 3. Carbon Number Distribution for the Acid and Base Fractions From SARA Chromatography Separation.

<u>2M</u>	<u>CLP Range</u>	<u>Bases</u>		<u>Acids</u>	
		<u>LRUV</u>	<u>Typical Structural Nitrogen Analogs</u>	<u>LRUV</u>	<u>Typical Structural Nitrogen Analogs</u>
- 5	6-12	Pyridines, Anilines		--	--
- 7	8-13	Azaindanes		--	--
- 9	9-15	Dihydroquinolines, Indole		--	--
-11	9-15	Quinolines		--	--
-13	11-17	Phenylpyridines		--	--
-15	12-19	Azafluorenes		12-20	Carbazoles
-17	13-19	Acridines		14-20	Phenylindoles
-19	14-21	Benzo[ghi]azafluorenes		14-22	Benzo[def]carbazoles
-21	15-21	Azapyrenes		16-24	Benzocarbazoles
-23	17-26	Benzacridines		18-24	Phenylcarbazoles
-25	17-26	Benzo[ghi]azafluoranthenes		--	--
-27	19-26	Benzazapyrenes		20-29	Dibenzocarbazoles
-29	21-26	Dibenzacridines		22-29	Naphthylcarbazoles
-31	21-26	Azaanthanthrenes		22-29	Naphthobenzo[def]carbazoles
-33	23-26	Dibenzazapyrenes		24-29	Anthracenocarbazoles
-35	23-27	Azacoronenes		26-29	Anthranylcarbazoles
-37	--	--		28-29	Anthracenobenzo[def]carbazoles
-39	--	--		28-30	Dinaphthocarbazoles

Table 2. SARA Chromatography Fractions, Weight Percent Distribution.

Chromatography Fraction Wt. % of CLP

Saturates 4.1

Aromatics 37.3

Acids 6.3

Bases 10.2

Neutral Nitrogen 3.9

Loss 7.4

Total Oil 68.0

Table 4. Compounds found in the nitrogen base fraction of Figure 2.

PEAK NUMBER	COMPOUND
1	SOLVENT (CARBON DISULFIDE)
2	PHENOL
3	CRESOL
4	CRESOL
5	TETRAHYDROQUINOLINE
6	QUINOLINE
7	6-METHYLTETRAHYDROQUINOLINE
8	METHYLQUINOLINE
9	ISOQUINOLINE
10	METHYLQUINOLINE
11	METHYLQUINOLINE
12	C ₂ -QUINOLINE
13	C ₂ -QUINOLINE
14	OCTAHYDRO-N-3-RING (OCTAHYDROACRIDINE)
15	METHYLOCTAHYDRO-N-3-RING (METHYLOCTAHYDROACRIDINE)
16	PHENANTHRIDINE + ACRIDINE
17	MEHTYLACRIDINE
18	AZAPYRENE
19	METHYLAZAPYRENE

Table 5. Carbon number range data for nitrogen heteromolecules in asphaltenes.

Asph.	Asph. A Carbon Number Range	Asph. B	Possible Structural Types
- 5	5-7	6	Pyridines
- 7	8-11	8-12	Azaindans
- 9	8-14	8-14	Dihydroquinolines; Indoles
-11	9-14	9-14	Quinolines
-13	11-16	11,12,14-17	Phenylpyridines
-15	11-19	11,12,14-19	Azafluorenes; Carbazoles
-17	13-20	14-20	Acridines
-19	14-20	14-19	Azabenzo[ghi]fluorenes
-21	15-21	15-20	Azapyrenes; Benzocarbazoles
-23	17-21	17-21	Benzacridines
-25	17-21	19-22	Azabenzo[ghi]fluoranthenes
-27	19-23	20-23	Azabenzopyrenes; Dibenzocarbazoles
-29	21-23	21-23	Dibenzacridines
-31	21-23	21,22	Azabenzoperylene
-33	23,24		Azadibenzopyrenes

Formulas derived by HRMS represent isomers and fragment ions as well as molecular ions.

Table 6. Identification and quantitation of selected peaks from nitrogen bases in light oils.

Table 8. TMS derivatized hydroxyl species in acid components from SARA separation.

Peak #	Compound	Wt. % of Base Fraction	Molecular Weights Phenol Series	Molecular Weights TMS Ether	Molecular Weights Indanol Series	Molecular Weights TMS Ether
1	2,6-Dimethylpyridine	0.5	94	166	134	206
2	2,4-Dimethylpyridine	2.2	108	180	148	220
3	2,3,6-Trimethylpyridine	3.5	122	194	162	234
4	3,5-Dimethylpyridine	1.5	136	208	176	248
5	Aniline	6.4	150	222	190	262
6	2-Methylaniline	12.8	164	236		276
7	4-Methylaniline	8.1				
8	3-Methylaniline	15.1				
9	Quinoline	7.6				

Table 7. Hydroxyl distribution in solvent separated fractions determined by TMS derivatization.

Fraction	% H as OH ±5%	% O as OH ±10%	Molecular Weights Acenaphthanol Series	Molecular Weights TMS Ether	Molecular Weights Fluorenol Series	Molecular Weights TMS Ether
Oils	1.2	67	170	242	196	268
Asphaltenes	2.0	43	184	256	210	282
Asphaltene Acid/Neutral	2.0	44	198	270	224	296
Asphaltene Base	1.5	49	212	284	238	310
Preasphaltenes	3.0	35	226	298	252	324
			240	312	266	338
			254	326	280	352

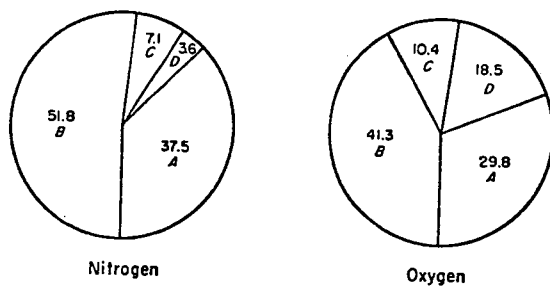


Figure 1. Atom weight percent distribution of heteroatoms. A) Oils, B) Asphaltenes, C) Preasphaltenes, and D) Ash.

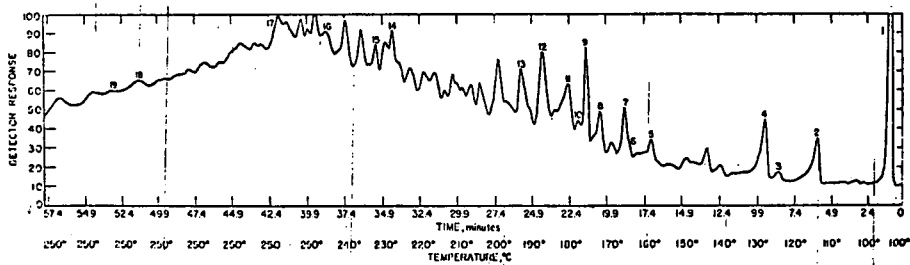


Figure 2. Gas chromatogram of base fraction from a coal liquefaction product. Table 4 identifies major components.

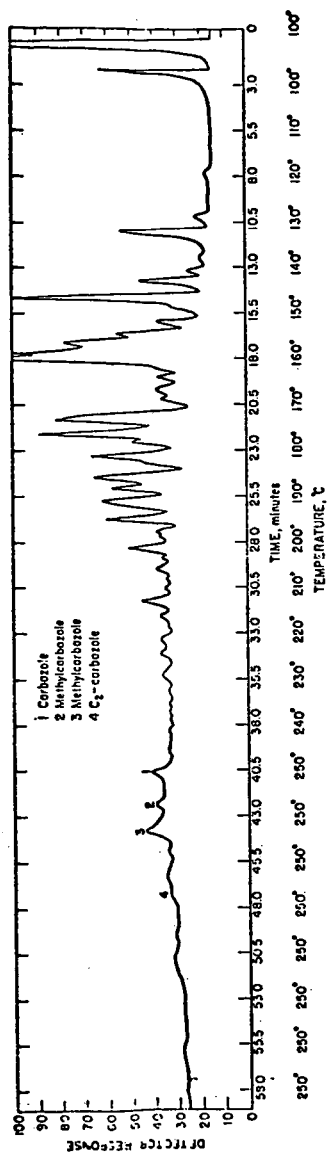


Figure 3. Gas chromatogram of acid fraction from a coal liquefaction product.

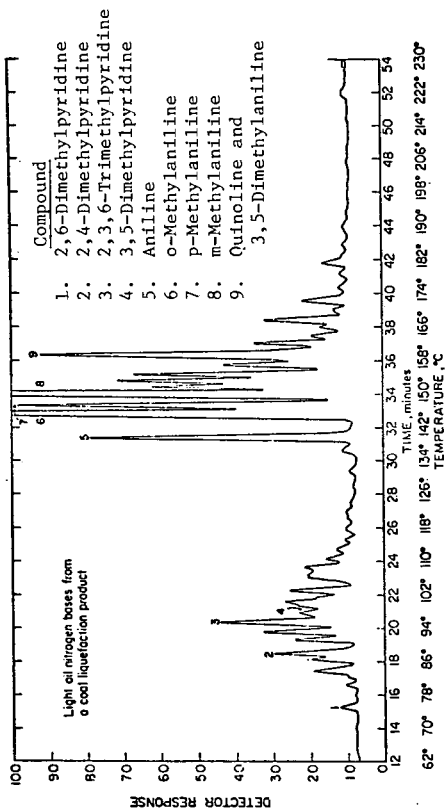


Figure 4. Gas chromatogram of nitrogen bases from a light oil.

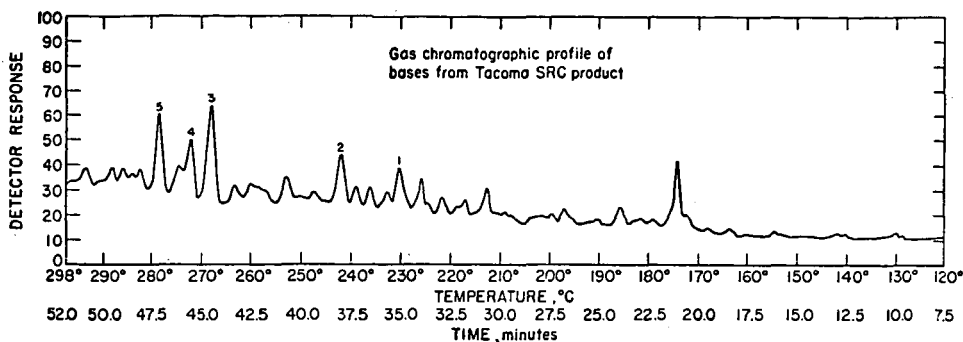


Figure 5. Gas chromatogram of nitrogen bases from an SRC recycle solvent. 1) N-3 ring, e.g. acridine, 2) methyl-N-3-ring, 3) azapyrene, 4) and 5) methylazapyrene.

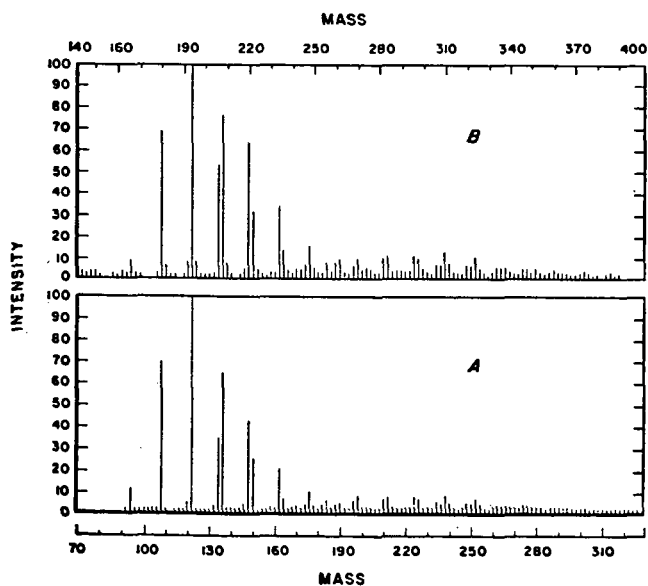


Figure 6. Mass spectrum of acids before (A) and after (B) TMS derivatization. Note change in mass scale.